

Field-induced Monoclinic Phase in $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$

B. Noheda, D.E. Cox, G. Shirane (BNL, Physics), R. Guo, B. Jones and L.E. Cross (Penn. State U.)

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The ferroelectric $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) system exhibits outstanding electromechanical properties close to the nearly vertical phase boundary between the tetragonal and rhombohedral regions of the phase diagram close to $x = 0.50$. [1] In the present work experimental evidence of an enhanced elongation along [001] for rhombohedral PZT and along [101] for tetragonal PZT ceramic disks revealed by high-resolution x-ray diffraction measurements after the application of an electric field is presented. This experiment was originally designed to address the question whether poling in the MPB region would simply change the domain population in the ferroelectric material, or whether it would induce a permanent change in the lattice constants. As shown below, the measurements reveal a series of changes of the in the peak profiles from the differently oriented grains in one sweep and provide key information about the PZT problem. The results demonstrate the existence of local monoclinic disorder in both the rhombohedral and tetragonal PZT compositions, and support the proposed model for the MPB. [2]

$\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ceramic samples with $x = 0.36, 0.42, 0.45, 0.46, 0.47, 0.48, 0.50$ and 0.52 were prepared by conventional solid-state reaction techniques. The sintered ceramic samples were ground to give parallel plates. Silver electrodes were applied to both surfaces of the annealed ceramic samples and air-dried. Disks of all compositions were poled under a DC field of 20 kV/cm at 125°C for 10 min. and then field-cooled to near room temperature. The electrodes were then removed chemically.

Several sets of high-resolution synchrotron x-ray powder diffraction measurements were made at X7A. A Ge(111) double-crystal monochromator was used in combination with a Ge(220) analyser, with a wavelength of about 0.8 \AA . In this configuration, the instrumental resolution, $\Delta 2\theta$, is an order-of-magnitude better than that of a conventional laboratory instrument (better than 0.01° in the 2θ region $0-30^\circ$). The poled and unpoled pellets were mounted in symmetric reflection geometry and scans made over selected peaks in the low-angle region of the pattern. The diffractograms of the poled and unpoled samples show distinctive features for both the rhombohedral and tetragonal compositions. PZT with $x = 0.48$, that at room temperature is just in the monoclinic-tetragonal boundary, after poling presents clear monoclinic features. This can be seen in **Figure 1** (top row) where it is shown that (111) and (202) that were already broad in the unpoled sample, indicating an incipient monoclinicity, are clearly split after poling. The (200) reflections shows the expected change in the (002)/(200) intensity ratio after poling due to the domain formation but the absolute no shift in the peak position indicates an absence of elongation along the $\langle 001 \rangle$ directions. In a rhombohedral composition as $x = 0.42$ (bottom of **Figure 1**) the poling broaden the (h00) and (hh0) reflections, and the expected change in the intensity ratios in the (111) reflections but no peak shift is observed along the polar [111] direction. The effect of the electric field is clearly observed, however, as a large shift of the (h00) reflections. The difference in the peak shifts for the different reflections means that we are measuring at once the different response of the differently oriented grains respect to the applied field. So, although the features after poling are still apparently rhombohedral, it is not possible to index the whole observed pattern either in the rhombohedral symmetry or in any other. These data show then that the changes induced in the unit cell after the application of an electric field do not increase either the rhombohedral or the tetragonal strains, but induce elongation along the directions that would produce the monoclinic distortion. This induced monoclinic distortion is retained after the suppression of the field. [3]

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References: [1] B. Jaffe *et al.*, "Piezoelectric Ceramics", Academic Press, London (1971). [2] B. Noheda *et al.* "Tetragonal-to-monoclinic phase transition in a ferroelectric perovskite", *Phys. Rev. B*, **61**, p. 8687-8695 (2000). [3] R Guo *et al.* " Origin of the high piezoelectric response in PZT", *Phys. Rev. Lett.*, **84**, p. 5423-5426 (2000).

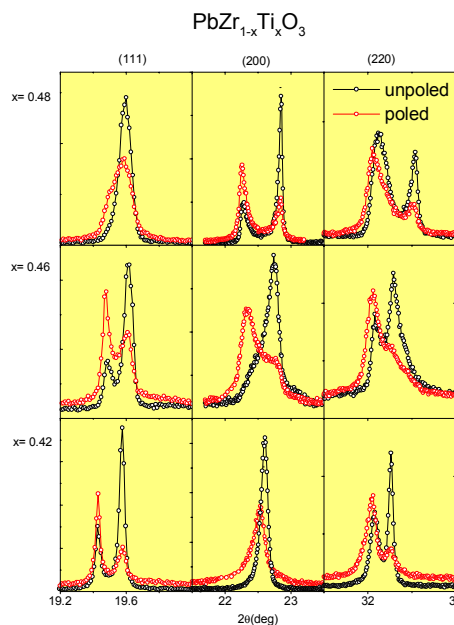


Figure 1. Comparison of the (111), (200) and (220) pseudo-cubic reflections for the poled and unpoled ceramic samples of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ with $x = 0.42, 0.46$ and 0.48 .